

DESCRIPTION

The present invention relates to a method for the production of a homogeneous cellular solution which contains N-methylmorpholine-N-oxide monohydrate as a solvent.

The dissolving of cellulose in N-methylmorpholine-N-oxide (NMMNO) monohydrate at temperatures above its melting point of 72 °C is known. his dissolving procedure runs very slowly, since, conditioned by the size of the solvent molecules and the high viscosity of the solution, the diffusion speed is very low. Through highly resolved cellulose obtained by fine grinding, high solution temperatures, and strong shear fields, the dissolving of the cellulose accelerates. In spite of the energy consumption connected with this, the speed of dissolving of the cellulose prepared in this way is insufficient.

The dissolving procedure is significantly improved if the cellulose is dispersed in approximately 60 % aqueous NMMNO solution and the excess water is distilled off above 85 °C with vacuum and stirring and simultaneous dissolving of the cellulose (Soviet Patent 994587).

Furthermore, adding the cellulose at 20 to 70 °C to an aqueous NMMNO solution in a bath ratio of 1:4 to 1:120, homogenizing it in the shear field, and reducing the bath ratio to 1:2.5 to 1:7 by pressing or centrifuging is also known. The "solid" suspension obtained is fed to an extruder with a degassing zone after drying and converted into a homogeneous solution at temperatures between 75 and 120 °C (German Democratic Republic Patent 2 26 573). The method has the disadvantage that it is only suitable for polymer solutions having a cellulose content of more than 16 mass-percent, since suspensions with a bath ratio above 1:7 flow and separate.

Furthermore, elevating the solubility of cellulose in aqueous NMMNO solution by a hydrothermic pre-treatment is known (German Democratic Republic Patent 2 98 789).

Finally, producing solutions of cellulose in aqueous tertiary aminoxides in one step, by continuously supplying a suspension of cellulose in the aqueous aminoxide solution to a thin layer evaporator and evaporating water with vacuum and elevated temperature until the cellulose goes into solution is known (European Patent 356 419). The disadvantages of this method are that once a thin layer evaporator is laid out, it has little variability in the parameters and cannot always react sufficiently to the different reactivities of various pulp provenances. Furthermore, the shear field of such an evaporator is very low and therefore the occurrence of gel particles in the solution obtained is possible. These gel particles, which are made of cellulose particles swollen up in NMMNO monohydrate, may lead to large problems in the filtration of the solution.

It may be inferred from all of the methods described that permissible dissolving times and sufficient homogeneity of the cellulose solution may only be achieved if the cellulose is added to aqueous NMMNO solutions of approximately 60 % and the concentration of the solutions to monohydrate (86.7 mass-percent NMMNO) from this relatively highly viscous suspension/solution is performed.

The present invention has the object of providing a method for the production of a homogeneous cellulose solution containing N-methylmorpholine-N-oxide monohydrate as a solvent with improved economic efficiency. A method for the production of a homogeneous solution of cellulose in N-methylmorpholine-N-oxide monohydrate is particularly to be provided in which the removal of significant quantities of water from the cellulose suspension in aqueous NMMNO used

for solution production is avoided. The dissolving of the cellulose in the solvent is particularly to be accelerated and simplified without significant intensification of the physical solution conditions. Finally, a method for the production of a homogeneous cellular solution with N-methylmorpholine-N-oxide monohydrate as a solvent is to be provided in which the dissolving process requires less energy use. Further advantages of the method according to the present invention arise from the following description.

This object is achieved according to the present invention with the method initially described in that a) cellulose is enzymatically pretreated with cellulase in an amount in a range of 0.1 to 10 mass-percent, in relation to cellulose, in an aqueous bath at temperatures between 20 and 70 °C and a pH value between 3 and 10, b) the pretreated cellulose is separated from the bath, and c) the separated cellulose is added to a melt made of N-methylmorpholine-N-oxide and water with a mole ratio N-methylmorpholine-N-oxide to water in the range from 1:1.2 to 1:0.8 and sheared until completely dissolved.

Surprisingly, it has been shown that dissolving cellulose in N-methylmorpholine-N-oxide monohydrate is made significantly easier if the cellulose is enzymatically pretreated according to the present invention. The pretreated cellulose may therefore be dissolved directly in the melt of the NMMNO monohydrate, which may contain water or NMMNO in a slight excess, without having to take the detour via an aqueous NMMNO solution with a high water content (e.g. 40 % water). In the method according to the present invention, comparatively little water is to be evaporated in step c). Due to this and to the significant reduction of the dissolving time for the cellulose, reduction of the energy consumption and the outlay for apparatus for the dissolving step results.

According to the preferred embodiment of the method according to the present invention, a concentrate obtained by concentration of the spinning bath arising during the spinning of the cellulose solution is used in step c). The concentration of the spinning bath, e.g. through evaporation in a multistage evaporation facility directly up to the monohydrate or even further, may be performed using significantly less energy and more carefully for the NMMNO than if the concentration from, for example, 60 to 87 mass-percent NMMNO occurs in the dissolving step from the highly viscous cellulose suspension and/or solution. The concentrate is expediently concentrated to at least 86.7 mass-percent NMMNO, i.e. up to at least the monohydrate stage. The greatest possible concentration appears expedient if the cellulose separated in step b) still contains a significant proportion of moisture. In this case, the cellulose will be introduced into a melt having as little water as possible, whose mole ratio NMMNO:H₂O is expediently 1:<1.

The dissolving of the cellulose in step c) is expediently performed at a temperature in the range from 72 to 95 °C. The temperatures most preferred lie between 80 and 90 °C.

The cellulose suspension is preferably degassed under vacuum during the dissolving procedure. The small quantities of water possibly to be removed in step c) are thus removed rapidly while preserving the solvent.

The pre-treatment is preferably performed with a cellulase content in the bath in the range from 0.5 to 3.0 mass-percent. The preferred pre-treatment temperature is in the range from 30 to 60 °C. In general, the pre-treatment is performed with a bath ratio of cellulose/water in the range from 1:3 to 1:30. The pH value is preferably in the range from 4.5 to 8. The separation of the enzymatically

pretreated cellulose from the bath may, for example, be performed by pressing or centrifuging.

In order to increase the effectiveness of the enzymatic pre-treatment, the cellulose may be whipped in water with shearing before the pre-treatment. The cellulases may already be contained in the bath during this initial step or they may be added only after whipping the bath. Through the initial step, the enzymatic activation of the cellulose is improved and the duration of the enzymatic pre-treatment is reduced. The duration of the enzymatic pre-treatment preferably lies in the range from 0.2 to 3 hours, particularly in the range from 0.75 to 2.0 hours. Commercially obtainable cellulases, e.g. Rucolase from the firm Rudolph-Chemie or Roglyr-1538 from the firm Rotta GmbH, may be used as the enzyme.

The bath separated in step b) is expediently recycled in step a) after replenishment of the enzyme consumed, which minimizes the costs for the enzyme. The cellulose, which is largely removed from the bath, is continuously or discontinuously introduced into the melt made of NMMNO and H₂O. The homogeneous solution obtained may be used directly for spinning into threads.

The present invention is described in more detail by the following examples and the comparative examples.

Examples 1 to 6

5 kg of a spruce sulfite pulp (α -cellulose content 96.5 %, Cuoxam DP [degree of polymerization] 630 and/or 431) was whipped in a heatable turbo slusher in water in a bath ratio of 1:5 to 1:20, heated to temperature between 30 and 60 °C, adjusted to pH values between 4.5 and 8 with diluted sulfuric acid and/or sodium hydroxide with stirring, had 0.5 to 3 mass-percent enzyme, in relation to f-cellulose,

added to it, and was treated for a duration of 0.75 to 2 hours. The treatment conditions for the individual examples are indicated in the table. The bath containing the enzyme was largely separated from the cellulose by centrifuging or pressing (water content = 50 %). The bath was used again in the turbo slusher after replenishment of the water and enzyme losses.

Example	DP before	Enzyme	% Enz.	bath ratio	pH	°C	min	DP after
1	632	Rucolase ¹	3	1:20	4.5	52	60	612
2	632	Roglyr 1538 ²	1	1:5	5.0	55	45	609
3	632	SP 424 ³	3	1:10	5.0	30	120	605
4	430	SP 424	2	1:10	5.0	55	60	385
5	430	SP 640	0.5	1:15	8.0	60	90	402
6	430	SP 431	2.5	1:20	6.0	55	60	390

¹product of the firm Rudolph Chemie

²product of the firm Rotta GmbH

³experimental product of the firm Novo Nordisk

It is obvious from the table that the degradation of the degree of polymerization under the conditions of the enzymatic pre-treatment was relatively low.

Example 7

888 g NMMNO hydrate melt (mole ratio NMMNO:H₂O = 1:0.9; refraction index at 50 °C n = 1.4788) was placed in a laboratory kneader having a delivery screw and 167 g of the cellulose obtained according to example 1 (water content 40 %) was added. After 5 min of stirring under vacuum of 20 mbar, 1 kg of a homogeneous, yellow polymer solution which is free of air bubbles was obtained, which was made of 10 % cellulose and 90 % NMMNO monohydrate with a refraction index at 50 °C of 1.4810.

The celluloses obtained from examples 2 to 6 may be converted in an analogous way in similarly short times into homogeneous polymer solutions.

Example 8

40 g/min of pretreated cellulose (water content 37.5 %) according to example 3 was continuously supplied to a double screw extruder (DSE, screw diameter 25 mm) via a balance. 219 g/min aminoxide melt (mole ratio NMMNO:H₂O = 1:0.9) was metered via a feed pump into the first zone of the DSE, which was heated to 85 °C all the way through. After mixing of both components, the mixture reached the degassing zone, where it was degassed under vacuum at 15 to 20 mbar and excess water was removed in a quantity of 9 g/min. At an average dwell time of 5 min, 250 g/min of homogeneous polymer solution (refraction index $n = 1.4794$ at 50 °C) continuously left the DSE. The solution comprised 10 % cellulose and 90 % NMMNO hydrate (mole ratio NMMNO:H₂O = 1:1.1).

Example 9

Analogously to example 8, 48 g/min of cellulose pretreated according to example 6 (water content 37.5 %) was supplied to the DSE, mixed with 216 g/min aminoxide melt (mole ratio NMMNO:H₂O = 1:0.9), and degassed, with simultaneous removal of water at 14 g/min. 250 g/min of homogeneous polymer solution (refraction index $n = 1.4813$ at 50 °C) with the composition 12 % cellulose and 88 % aminoxide hydrate (mole ratio NMMNO:H₂O = 1:1.05) was continuously removed from the extruder.

Comparative example 1

As in example 7, 888 grams aminoxide-hydrate melt (mole ratio NMMNO:H₂O = 1:0.9; refraction index at 50 °C $n =$

1.4788) was placed in a laboratory kneader with a delivery screw at 85 °C. nstead of the pretreated cellulose, 167 g spruce sulfite cellulose (α -cellulose content 96.5 %, Cuoxam DP 630) was added, which was whipped in a heatable turbo slusher in water in the bath ratio 1:15 and then dewatered to a water content of 40 %. The mixture was stirred under vacuum of 20 mbar. It displayed the following appearance after

1 hr.: significant portions are swollen;
6 hr.: significant portions are dissolved;
12 hr.: isolated undissolved fiber residue.

Comparative example 2

The operation was in the same as in comparative example 1, however the cellulose was not whipped, but subjected to extremely fine milling in a Condux mill, and added dry to the NMMNO monohydrate melt. The appearance of the mixture during stirring under vacuum of 20 mbar was, after

1 hr.: small portions were swollen;
6 hr.: significant portions were swollen, small portions were dissolved;
12 hr.: significant portions were still undissolved.

CLAIMS

1. A method for the production of a homogeneous cellulose solution, which contains N-methylmorpholine-N-oxide monohydrate as a solvent,

characterized in that
 - a) cellulose is enzymatically pretreated with cellulase in an amount in a range of 0.1 to 10 mass-percent, in relation to cellulose, in an aqueous bath at temperatures between 20 and 70 °C and a pH value between 3 and 10,
 - b) the pretreated cellulose is separated from the bath, and
 - c) the separated cellulose is added to a melt with a mole ratio N-methylmorpholine-N-oxide to water in the range from 1:=1.2 to 1:=0.8 and sheared until completely dissolved.
2. The method according to Claim 1,

characterized in that

in step c), a concentrate obtained by concentrating the spinning bath arising during the spinning of the cellulose solution is used.
3. The method according to Claim 2,

characterized in that

the concentrate is concentrated to at least 86.7 mass-percent N-methylmorpholine-N-oxide.
4. The method according to one of Claims 1 to 3,

characterized in that

the step c) is performed at a temperature in the range from 72 to 95 °C.

5. The method according to one of Claims 1 to 4,

characterized in that

the cellulose suspension is degassed under vacuum during the dissolving procedure.

6. The method according to one of Claims 1 to 5,

characterized in that

the pretreatment is performed with a cellulose [sic] content in the range from 0.5 to 3.0 mass-percent.

7. The method according to one of Claims 1 to 6,

characterized in that

the pretreatment is performed at a temperature in the range from 30 to 60 °C.

8. The method according to one of Claims 1 to 7,

characterized in that

the pretreatment is performed with a bath ratio cellulose/water in the range from 1:3 to 1:30.

9. The method according to one of Claims 1 to 8,

characterized in that

the pretreatment is performed at a pH value in the range from 4.5 to 8.

10. The method according to one of Claims 1 to 9,

characterized in that

the cellulose is whipped before the enzymatic pretreatment with shearing in water.

11. The method according to one of Claims 1 to 10,

characterized in that

~~the bath separated in step b) is recycled after~~
replenishment of the enzyme consumed in step a).

Request for examination has been filed pursuant to § 44
Patent Code

(54) METHOD FOR THE PRODUCTION OF A HOMOGENEOUS CELLULAR
SOLUTION

(57) Method for the production of a homogeneous cellular solution, which contains N-methylmorpholine-N-oxide monohydrate as a solvent, characterized in that a) cellulose is enzymatically pretreated in an aqueous bath at temperatures between 20 and 70 °C and a pH value between 3 and 10 with cellulase in an amount in a range of 0.1 to 10 mass-percent, in relation to cellulose, b) the pretreated cellulose is separated from the bath, and c) the separated cellulose is added to a melt with a mol ratio N-methylmorpholine-N-oxide to water in the range from 1:1.2 to 1:0.8 and sheared until completely dissolved. During the method, the removal of a significant amount of water from the cellulose suspension in aqueous NMMNO used for the production of the solution is avoided. The accelerated and simplified dissolving of the cellulose is performed without significant intensification of the physical solution conditions.